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(54) Title: POLYESTER ARTICLE			
(57) Abstract A polyester article is described which comprises a polyester polymer produced using a catalyst obtainable by reacting an alkyl titanate or an alkyl zirconate, an alcohol, a 2-hydroxy carboxylic acid and a base. The article preferably takes the form of a film or a bottle. Also described is a process for the production of the article.			

POLYESTER ARTICLE

The present invention relates to a polyester article, particularly in the form of a film or a container, and more particularly to a polyester article comprising polyester produced using a specific titanium or zirconium catalyst.

The use of polyesters, particularly polyethylene terephthalate or copolymers thereof (often referred to collectively as polyethylene terephthalate or PET), for the manufacture of packaging material, such as films, bottles and other containers, is well known. In the case of bottles for containing drinks, such as carbonated soft drinks and mineral water, these are normally fashioned from the polyester, typically in the form of polymer chip, using a two stage process. In the first stage of the process, a bottle preform is made from the polyester by injection moulding and in the second stage this bottle preform is heated to an appropriate temperature, e.g. using infra red radiation, and then blown using compressed air into a mould which is the final shape of the bottle. The blow moulding process causes biaxial orientation of the polyester to occur in selected regions of the bottle, such as the cylindrical main wall, and this endows the bottle with greater strength allowing it to resist deformation during use. A preferred blow moulding process is a stretch blow moulding process in which an inner mandrel is moved into the preform along the axis thereof before and/or simultaneously with the introduction of the compressed air so as to facilitate the stretching of the bottle preform in the axial direction.

It is well known to prepare polyester in a two stage process. In the first stage 'monomer' is produced at an elevated temperature typically in the range from 150 to 285°C by reacting a dicarboxylic acid with a glycol (direct esterification) or alternatively by reacting an alkyl ester of a dicarboxylic acid with a glycol (ester interchange or transesterification). A catalyst such as manganese acetate or zinc acetate is normally employed in the ester interchange reaction, whereas direct esterification can be carried out in the absence of a catalyst. In the second stage of

into pellets. These pellets are usually of amorphous polymer owing to the rapid cooling process.

The prepolymer pellets are then subjected to solid state polymerisation which involves heating the pellets, typically to a temperature of around 210 to 240°C, under partial vacuum or in an inert gas flow. The solid state polymerisation can be carried out in fluidised bed reactors, in tumbling chip reactors or in continuously operating fixed bed reactors, and is typically continued until the IV of the polymer is about 0.7 to 0.9 dl/g.

As mentioned above, the prepolymer pellets generated in the melt phase polymerisation process are amorphous, and as such tend to soften and stick together (sinter) at the kinds of temperatures which are needed to create a satisfactory polymerisation rate in the solid state. To avoid this problem, the amorphous prepolymer pellets are usually crystallised prior to solid state polymerisation by heating the pellets to a temperature which is slightly below that prevailing in the solid state polymerisation. The crystalline prepolymer softens at higher temperatures than the amorphous material and so the problem of the prepolymer pellets sticking together at the temperatures encountered in the solid state polymerisation process is avoided.

Titanium compounds, such as alkyl titanates, have been used as polyester catalysts, both for monomer formation and polycondensation. Unfortunately, however, titanium catalysts often result in the production of a polymer having a relatively high haze due to deactivation of the titanium catalyst and the precipitation of inorganic titanium compounds such as titanium dioxide. As a result, films and containers made from the polymer are often unacceptable due to the level of haze. The aforementioned deactivation of the titanium catalyst can also result in a reduction in the catalytic efficiency thereof. Furthermore, titanium catalysts often yield polymers which are yellow in appearance and thus unsuitable for making films and bottles. Yellowing of the polymer is particularly undesirable when the polymer is to be used for making bottles where a water white, transparent polymer is required.

The present invention also includes the preforms from which bottles can be made, particularly injection moulded bottle preforms. Thus, according to a further aspect of the present invention there is provided a polyester bottle preform comprising a polyester polymer produced using a catalyst obtainable by reacting an alkyl titanate or an alkyl zirconate, an alcohol, a 2-hydroxy carboxylic acid and a base.

Injection blow moulded bottles are made in a two stage process. In the first stage of the process a bottle preform is produced from the polyester polymer by injection moulding and in the second stage the preform is heated to an appropriate temperature, e.g. using infra red radiation, and then blow moulded to make the final bottle product. Injection stretch blow moulded bottles are made by the same process as injection blow moulded bottles except that the preform is also axially stretched using a mandrel before and/or during the blow moulding process.

The preform takes the form of a miniature bottle, generally being a cylinder closed at one end and having a length about a third and an external diameter about a quarter of the final bottle. For example, a bottle having a capacity of 1.5 litres will typically be about 30 cm long and have an external diameter of about 8 to 12 cm. The intermediate preform for such a bottle would typically be about 10 to 15 cm long and about 3 to 4 cm in external diameter.

A suitable polyester polymer for making containers and particularly bottles is a partially aromatic polyester and particularly a polyester which is substantially derived from an aromatic diacid (or an ester thereof) and an aliphatic (including cycloaliphatic) diol.

A preferred partially aromatic polyester for making containers and particularly bottles is one which comprises at least 50 mole %, preferably at least 70 mole %, of ethylene terephthalate residues, i.e. residues derived from the reaction of terephthalic acid or an ester thereof, e.g. dimethyl terephthalate, and ethylene glycol. The polyester may also contain residues derived from ethylene isophthalate, ethylene naphthalate,

acid as a percentage of the total dicarboxylic acid derived units in the polymer will be in the range of from 1.0 to 12.0 mole %, and particularly advantageous results may be attainable using proportions in the range of from 1.5 to 4.0 mole %, especially 1.8 to 3.0 mole %.

The modified polyethylene terephthalate polymer may also include a small proportion of diethylene glycol residues to replace some of the usual monoethylene glycol residues. The polymerisation process which is used to prepare polyethylene terephthalate for bottles will usually result in the incorporation of some polyethylene glycol residues in the polymer, particularly diethylene glycol residues and to a lesser extent triethylene glycol residues. In a continuous polymerisation process, the proportion of polyethylene glycol residues incorporated in the polymer will typically be of the order of 1.5 to 2.5 mole % based on the total glycol residues in the polymer. (The di- and tri-ethylene glycol residues may be formed by the linking of chains terminated by glycol residues as well as by etherification of the ethylene glycol monomer, so there is not necessarily any free di- or tri-ethylene glycol formed during the reaction.) However, if desired, additional diethylene glycol residues may be incorporated into the polymer by adding diethylene glycol as a monomer.

When the polyester article of the invention is a bottle, the polyester polymer from which it is formed will typically have an Intrinsic Viscosity (IV) in the range of from 0.70 to 0.90 (as measured on a 1% w/v solution of the polymer in *o*-chlorophenol at 25°C). A particularly useful range for the IV is from 0.72 to 0.85. Preferred polyester polymers for converting into bottles will also have a haze value of less than 9, particularly less than 8 and especially less than 6. By haze we mean the percentage of light which deviates by more than 2.5° on average in the forward direction as measured using a Gardner Pivotal Sphere Hazemeter on a polyester plaque 100 mm in diameter and 4 mm thick.

The polyester film may be unoriented, or preferably oriented, for example uniaxially oriented, or more preferably biaxially oriented by drawing in two mutually perpendicular directions in the plane of the film to achieve a satisfactory combination of mechanical and physical properties. Simultaneous biaxial orientation may be effected by extruding a thermoplastics polymeric tube which is subsequently quenched, reheated and then expanded by internal gas pressure to induce transverse orientation, and withdrawn at a rate which will induce longitudinal orientation. Sequential stretching may be effected in a stenter process by extruding the thermoplastics material as a flat extrudate which is subsequently stretched first in one direction and then in the other mutually perpendicular direction. Generally, it is preferred to stretch firstly in the longitudinal direction, i.e. the forward direction through the film stretching machine, and then in the transverse direction. A stretched substrate film may be, and preferably is, dimensionally stabilised by heat-setting under dimensional restraint at a temperature above the glass transition temperature thereof.

When the polyester article of the invention is a film, the polyester polymer from which it is formed will typically have an IV in the range of from 0.5 to 0.8, preferably in the range of from 0.6 to 0.65, and particularly in the range of from 0.61 to 0.63. The polyester surprisingly exhibits a low IV drop on film extrusion, preferably less than 0.04, more preferably in the range from 0.001 to 0.03, particularly 0.005 to 0.002, and especially 0.01 to 0.015.

In a particularly preferred embodiment of the invention, the polyester used in the manufacture of the film exhibits a colour "b" value (i.e. yellowness value) in the range of from -6 to +6, more preferably -3 to +3, and especially -1 to +2.

In a preferred embodiment of the invention, the polyester film is transparent, exhibiting high optical clarity and low haze, preferably having a wide angle haze, being measured according to the standard ASTM D 1003-61, of <3%, more preferably <1%, particularly <0.5%, and especially <0.2%, preferably for a 125 μm thick film. The aforementioned optical characteristics can be suitably achieved by having little or no

The coating medium may be applied to an already oriented polyester film surface, but application of the coating medium is preferably effected before or during the stretching operation. In particular, it is preferred that the coating medium should be applied to the polyester film surface between the two stages (longitudinal and transverse) of a biaxial stretching operation.

The polyester film or additional coating layer(s), may conveniently contain any of the additives conventionally employed in the manufacture of polymeric films. Thus, agents such as dyes, pigments, voiding agents, lubricants, anti-oxidants, anti-blocking agents, surface active agents, slip aids, gloss-improvers, prodegradants, ultra-violet light stabilisers, viscosity modifiers and dispersion stabilisers may be incorporated into the film-forming (co)polyester and/or coating layer medium.

The catalyst which is used to produce the polyester polymer from which the polyester article of the present invention is made is obtainable by reacting, and preferably is the reaction product of, an alkyl titanate or an alkyl zirconate, an alcohol, a 2-hydroxy carboxylic acid and a base. A combination of an alkyl titanate and an alkyl zirconate may be used in the preparation of the catalyst if desired.

By the terms alkyl titanate and alkyl zirconate, we are intending to include compounds having substituted alkyl groups. The term also includes condensed products which are frequently represented by the formula $R^1O[M(OR^1)_nO]_nR^1$ in which M is titanium or zirconium and R^1 is an alkyl group, preferably containing from 1 to 6 carbon atoms. Preferably, n is less than 20 and more preferably is less than 10. Suitable condensed alkyl titanates and alkyl zirconates include the compounds known as polybutyl titanate, polyisopropyl titanate and polybutyl zirconate.

Preferred alkyl titanates and alkyl zirconates for preparing the catalyst have the formula $M(OR)_4$ in which M is titanium or zirconium and R is an alkyl group, preferably containing from 1 to 6 carbon atoms. Preferred alkyl titanates include tetramethyl titanate, tetraethyl titanate, tetrapropyl titanate, tetrakisopropyl titanate, tetrabutyl titanate and tetrahexyl titanate. Tetraisopropyl titanate is particularly

method, the alkyl titanate or zirconate is reacted with the 2-hydroxy carboxylic acid and the alcohol bi-product removed. The base is then added to this reaction product followed by the alcohol.

The amount of catalyst used in the production of the polyester from which the polyester article of the present invention is made will depend, inter alia, upon the titanium or zirconium content of the catalyst and also on whether the article is a film or a container. If the article is a container and particularly if it is a bottle, the amount of catalyst which is used in the preparation of the polyester polymer will usually be such as to provide from 2.5 to 100 ppm, preferably from 5 to 75 ppm, more preferably from 7.5 to 50 ppm, and especially from 7.5 to 30 ppm of titanium or zirconium atoms based on the weight of the polyester polymer which is finally produced. If the article is a film, the amount of catalyst which is used in the preparation of the polyester polymer will usually be such as to provide from 15 to 120 ppm, preferably from 15 to 100 ppm, more preferably from 20 to 30 ppm, and especially from 24 to 30 ppm of titanium or zirconium atoms based on the weight of the polyester polymer which is finally produced.

A mixture of any two or more of the titanium and zirconium catalysts described herein may be employed to produce the polyester polymer.

The titanium or zirconium catalyst may catalyse the esterification or ester interchange reactions used to produce monomer as well as the melt phase and optionally solid state polymerisation reactions which follow. Thus, the catalyst may be added before monomer formation so that it is at least catalysing the esterification or ester interchange reaction and perhaps also the polymerisation process which follows, or it may be added after monomer formation when it will serve to catalyse the polymerisation process only. Preferably, the catalyst is added before monomer formation.

In one embodiment of the present invention, the polyester from which the polyester article is made is produced by using the titanium or zirconium catalyst to

toning material is a cobalt (II) salt, such as cobalt acetate and cobalt acetate tetrahydrate, which will typically be added in an amount to provide from 19 to 60 ppm, preferably from 27 to 41 ppm, and more preferably from 31 to 36 ppm of cobalt based on the weight of the final polyester. Another suitable toning material is a combination of red and blue dyes. The red dye will preferably be added in an amount of from 1 to 15 ppm, more preferably from 1 to 10 ppm, and particularly preferably from 2 to 5 ppm based on the weight of the polymer. The blue dye will preferably be added in an amount of from 1 to 20 ppm, more preferably from 1 to 15 ppm, and particularly preferably from 3 to 8 ppm based on the weight of the polymer.

The toning material is preferably added after monomer formation, i.e. after the direct esterification or ester interchange reaction, and prior to the polycondensation reaction. The toning material is, however, preferably added after the phosphorus compound.

Sodium hydroxide may also be added to the reaction mixture, preferably prior to monomer formation and more preferably at the same time as the titanium or zirconium catalyst, in order to suppress the formation of diethylene glycol. If sodium hydroxide is incorporated in the reaction mixture, the amount which is added will preferably be such as to provide no more than 40 ppm, more preferably no more than 30 ppm and particularly preferably no more than 20 ppm of sodium based on the weight of the final polyester.

The present invention is now illustrated but not limited with reference to the following examples.

Example 1

The catalyst was prepared by dissolving citric acid monohydrate (132.5 g, 0.63 moles) in warm water (92.8 g) in a 1 litre fishbowl flask fitted with a stirrer, condenser and thermometer. To the stirred solution was slowly added tetraisopropyl titanate (72.0 g,

Example 2

The catalyst was prepared as described in Example 1.

A polyethylene terephthalate (PET) polymer was made using a batch terephthalic acid based route. The esterification vessel was charged with 59.3 kg of terephthalic acid, 1.2 kg isophthalic acid, 26 litres ethylene glycol and a solution of the titanium catalyst produced above (to give 24 ppm of Ti atoms). The mixture was heated to 265°C until all the reaction water had been distilled off. Phosphoric acid stabiliser was then added (to give 13.2 ppm of P atoms) and the reaction mixture transferred to an autoclave. Cobalt acetate tetrahydrate toner in ethylene glycol was added at this point to give 35.9 ppm of Co atoms. The reaction mixture was then heated to 280 to 290°C and melt polymerisation under vacuum occurred. The resulting PET polymer was glass clear, showed no signs of catalyst haze by dark field analysis, had an IV of about 0.63 (as estimated using the final torque of the autoclave stirring arm at 40 revs per minute (rpm)), and was suitable for making into a film. The colour of the polymer was also measured on a Colorgard System 45 using the Hunter scale (lh, ah, bh). The following results were obtained.

lh = 47.12; ah = 6.05; bh = 0.19

Example 3

The catalyst was prepared as described in Example 1.

A polyethylene terephthalate (PET) polymer was made using a batch terephthalic acid based route. The esterification vessel was charged with 59.3 kg of terephthalic acid, 1.2 kg isophthalic acid, 26 litres ethylene glycol and a solution of the titanium catalyst produced above (to give 24 ppm of Ti atoms). The mixture was heated to 265°C until all the reaction water had been distilled off. Phosphoric acid

lh = 67.9; ah = -0.78; bh = 18.49

Example 5

The catalyst was prepared as described in Example 1.

A polyethylene terephthalate (PET) polymer was made using a batch terephthalic acid based route. The esterification vessel was charged with 60.5 kg of terephthalic acid and 26 litres of ethylene glycol. The mixture was heated to 265°C until all the reaction water had been distilled off. Trisnonylphenyl phosphite stabiliser was then added (to give 13.6 ppm of P atoms) and once this was well mixed in, a solution of the titanium catalyst produced above was added (to give 30 ppm of Ti atoms). The reaction mixture was then transferred to an autoclave, heated to 280 to 290°C and melt polymerisation under vacuum occurred. The resulting PET polymer was slightly milky in appearance, had an IV of about 0.63 (as estimated using the final torque of the autoclave stirring arm at 40 revs per minute (rpm)) and was suitable for making into a film. The colour of the polymer was also measured on a Colorgard System 45 using the Hunter scale (lh, ah, bh). The following results were obtained.

lh = 66.43; ah = -2.03; bh = 20.82

Example 6

750 g of the PET polymer prepared in Example 1 was polymerised in the solid state at 213°C under a flow of nitrogen to yield a PET polymer having an IV of around 0.82 as measured by melt viscometry. This polymer was then made into a bottle using an injection stretch blow moulding technique.

Table 1

Example No.	Ti ppm	P ppm	Toner	IV	L*	a*	b*	lh	ah	bh
7	15	9.7	none	0.61	74.9	-1.85	19.1	69.3	-1.71	15.7
8	7.5	4.8	none	0.6	80.6	-2.48	12.2	76.0	-2.36	10.8
9	11.25	7.3	none	0.61	78.9	-1.88	19.3	73.3	-1.76	16.2

Table 2

Example No	Ti ppm	P ppm	Co ¹ ppm	red dye ppm ²	blue dye ppm ²	L*	a*	b*	lh	ah	bh
10	7.5	4.8	30.8	-	-	63.2	5.58	-3.09	56.4	4.91	-2.74
11	7.5	4.8	-	2	5	55.5	6.36	-12.3	48.4	5.34	-11.2
12	24	13.2	31.4	-	-	54.6	8.75	-3.88	47.5	7.36	-3.28

¹Co was added as cobalt acetate tetrahydrate in ethylene glycol.

²The red and blue dyes, Estofil SFBL (TM) and Estofil SRBL (TM) respectively, are available from Clariant UK Ltd. The dyes were added as a solution in ethylene glycol.

The above polymers were then polymerised in the solid state at 210°C under a flow of nitrogen to yield PET polymers having an IV of around 0.82 as measured by melt viscometry. In Examples 7, 8 and 9, samples of the PET polymers obtained after solid state polymerisation were made into plaques 100 mm in diameter and 4 mm thick and the haze values of the polymer plaques were then measured using a Gardner Pivotal Sphere Hazemeter. Haze values of 1.8, 1.6 and 2.2 were obtained for the polymers of Examples 7, 8 and 9. Finally, the PET polymers obtained after solid state polymerisation in Examples 7 to 11 were made into bottles using an injection stretch blow moulding technique. The final polymer of Example 12 was also suitable for making into a bottle.

Claims:

1. A polyester article comprising a polyester polymer produced using a catalyst obtainable by reacting an alkyl titanate or an alkyl zirconate, an alcohol, a 2-hydroxy carboxylic acid and a base.
2. A polyester article as claimed in claim 1 in the form of a container.
3. A polyester article as claimed in claim 2 wherein the container is a bottle.
4. A polyester article as claimed in claim 1 in the form of a film.
5. A polyester article as claimed in any one of claims 1 to 4 wherein the alkyl titanate or alkyl zirconate has the formula $M(OR)_4$ in which M is titanium or zirconium and R is an alkyl group containing from 1 to 6 carbon atoms.
6. A polyester article as claimed in any one of claims 1 to 5 wherein the polyester polymer is produced using a catalyst comprising the reaction product of an alkyl titanate, an alcohol, a 2-hydroxy carboxylic acid and a base.
7. A polyester article as claimed in any one of claims 1 to 6 wherein the alkyl titanate is tetraisopropyl titanate.
8. A polyester article as claimed in any one of claims 1 to 7 wherein the alcohol comprises at least two hydroxyl groups.
9. A polyester article as claimed in claim 8 wherein the alcohol is a dihydric alcohol.
10. A polyester article as claimed in claim 9 wherein the dihydric alcohol is ethylene glycol.
11. A polyester article as claimed in any one of claims 1 to 10 wherein the 2-hydroxy carboxylic acid is citric acid.
12. A polyester article as claimed in any one of claims 1 to 11 wherein the base is an inorganic base.
13. A polyester article as claimed in claim 12 wherein the inorganic base is sodium hydroxide.

25. A polyester article as claimed in claim 24 wherein the polyester polymer contains no more than 30 ppm by weight of sodium.
26. A polyester article as claimed in any one of the preceding claims wherein the polyester polymer has a colour "b" value in the range of from -6 to +6.
27. A polyester article as claimed in claim 4 wherein the film has a wide angle haze of less than 1%.
28. A process for the production of a polyester article which involves making use of a polyester polymer produced using a catalyst obtainable by reacting an alkyl titanate or an alkyl zirconate, an alcohol, a 2-hydroxy carboxylic acid and a base.
29. A polyester bottle preform comprising polyester polymer produced using a catalyst obtainable by reacting an alkyl titanate or an alkyl zirconate, an alcohol, a 2-hydroxy carboxylic acid and a base.
30. The use in the preparation of a polyester article of a polyester polymer produced using a catalyst obtainable by reacting an alkyl titanate or an alkyl zirconate, an alcohol, a 2-hydroxy carboxylic acid and a base.

INTERNATIONAL SEARCH REPORT

ANHANG

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

In diesem Anhang sind die Mitglieder
der Patentfamilien der in obenge-
nannten internationalen Recherchenbericht
angeführten Patentdokumente angegeben.
Diese Angaben dienen nur zur Unter-
richtung und erfolgen ohne Gewähr.

ANNEX

to the International Search
Report to the International Patent
Application No.

PCT/GB 97/01503 SAE 161711

This Annex lists the patent family
members relating to the patent documents
cited in the above-mentioned inter-
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ANNEXE

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

La présente annexe indique les
membres de la famille de brevets
relatifs aux documents de brevets cités
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Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche		Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
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